

Bimolecular reactions observed by femtosecond detachment to aligned transition states: Inelastic and reactive dynamics

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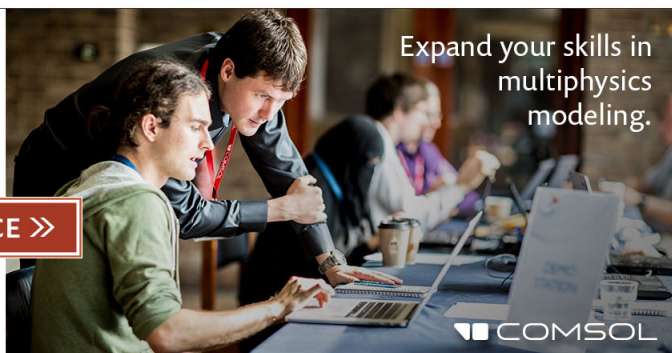
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Bimolecular reactions observed by femtosecond detachment to aligned transition states: Inelastic and reactive dynamics

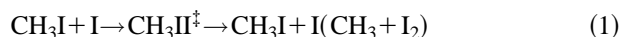
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With fs radical detachment and kinetic energy-resolved time-of-flight (KETOF) mass spectrometry, we are able to study the transition state dynamics of the bimolecular reaction $\text{CH}_3\text{I}+\text{I}$, inelastic and reactive channels; the collision complex is coherently formed (1.4 ps) and is long lived (1.7 ps). We also report studies of the dynamics of I_2 formation. Direct clocking of the CH_3I dissociation, hitherto unobserved, gives 150 fs for the C–I bond breakage time and 0.8 Å for the repulsion length scale. © 1996 American Institute of Physics. [S0021-9606(96)03241-2]

In this Communication, we report our first direct study of the femtosecond dynamics of the inelastic and reactive processes of the bimolecular reaction:



a general class of halogen-atom reactions with alkyl halides (RX) or hydrocarbons (RH).^{1–3} The reverse channel of radical reactions with halogen molecules is exoergic and has received considerable attention.^{4–6} In our experiments, the entire system is prepared on the reactive, *ground state* potential energy surface by direct launching of the wave packet of the collision complex $\text{CH}_3\text{I}^\ddagger$ at time zero. The concept is illustrated in Fig. 1(A). The translationally hot I atom is formed in 150 fs by detaching the CH_3 group in the direct dissociation of the moiety CH_3I [see below and Fig. 1(B)]. The reaction of $\text{CH}_3\text{I}+\text{I}$ is observed from the van der Waals (vdW) geometry of the dimer at the $\text{I}\cdots\text{I}$ and $\text{C}\cdots\text{I}$ internuclear distances of the transition state (TS). The product I atom is then monitored with a series of probe pulses and by gating the different product velocities. As with other real-time studies of bimolecular reactions,^{7–11} the approach allows for direct clocking of the complex with a limited impact parameter and relatively well-defined energy.

The potential energy surface (PES) has a late TS¹² for $\text{CH}_3\text{I}+\text{I}$ with a ~ 19 kcal/mol reaction barrier to form CH_3+I_2 .^{4–6} Depending on the translational energy of the I atom, the complex may be trapped in the vdW potential well in the transition state region, exchanges the energy between I and CH_3I , and finally decomposes into the $\text{CH}_3\text{I}+\text{I}$. Thus by monitoring the I atom buildup, the temporal behavior will reflect the nature of the transition state of the $\text{CH}_3\text{I}^\ddagger$ complex. This *inelastic* dynamical process is illustrated in Fig. 1(A) by the trajectory reflection.

We observe two distinct collisional times for the inelastic dynamics of the $\text{CH}_3\text{I}^\ddagger$ complex: a *delayed* time (~ 1.4 ps) and then an *exponential-rise* time (~ 1.7 ps). The delayed response elucidates the origin of the coherent process in the entrance channel and toward the transition state of the complex $\text{CH}_3\text{I}^\ddagger$ while the rise time gives the measured lifetime

of the complex (1.7 ps) at the collisional energy of 1.29 kcal/mol. By monitoring product I_2 , the reactive channel was found to be very fast, within 500 fs. This channel is the result of the “four-center” bimolecular reaction process. We also report here the dynamics of the unimolecular dissociation (150 fs) for $\text{CH}_3\text{I}^\ddagger\rightarrow\text{CH}_3+\text{I}$ and determine the terminal velocity of its fragments. Molecular dynamics (MD) simulations are discussed.

The fs laser system and the molecular beam apparatus used have been described previously.¹¹ The pump pulse (277 nm) initiates the CH_3I dissociation and the probe pulses (around 304 nm) detect the free iodine atoms (2+1 REMPI). For KETOF experiments, the pump polarization was fixed parallel to the TOF-MS (z) axis and perpendicular to the probe polarization. We performed the time-resolved experiments by gating the velocity range of interest, as we did in other studies.¹³ The I_2 was detected in the *B* state by a 1+1 REMPI scheme; 304 nm pump and 277 nm probe. Calibration of $t=0$ and system response function was made *in situ*.¹¹ The molecular beam conditions were established by varying the time delay between the fs laser pulses and the pulsed valve opening. A gas mixture expansion containing methyl iodide vapor (-25°C , ~ 40 Torr) with He gas (~ 800 Torr) was made and, as shown in Fig. 2, the leading edge only contains the monomer mass peak and the one which is slightly behind includes the monomer and *only* the dimer mass peak. We have studied the mass spectra for a variety of concentrations and these studies will be detailed later.

UNIMOLECULAR DISSOCIATION

The dissociation of methyl iodide from the A band absorption ($n\rightarrow\sigma^*$ transition) has been extensively studied, both theoretically¹⁴ and experimentally.¹⁵ Photofragment anisotropy measurements,¹⁶ picosecond real-time studies,¹⁷ and Raman scattering of dissociating CH_3I (Kinsey's group)^{14,15} have shown that the dissociation time is less than 500 fs. Here, we are able to directly clock the fs dissociation dynamics. The TOF mass spectrum and I^+ KETOF distribution are

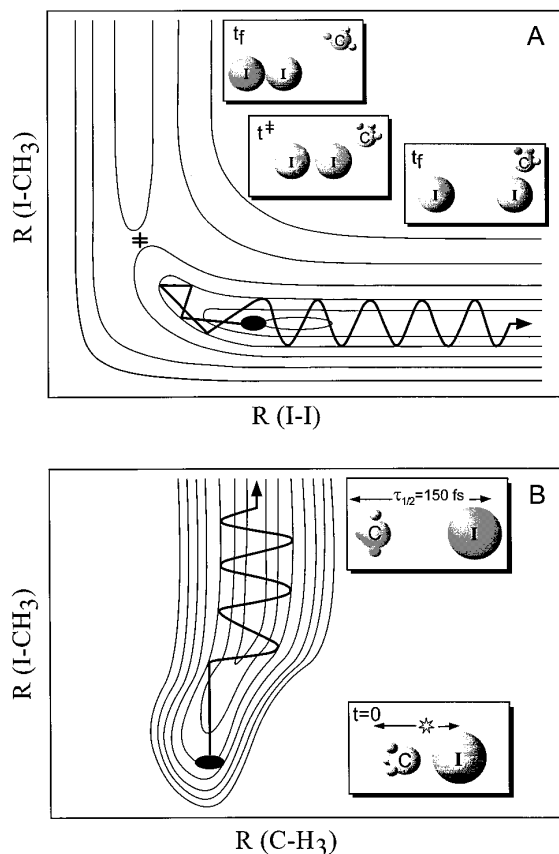


FIG. 1. Upper panel: A contour PES map for the full-collision, bimolecular $\text{CH}_3\text{I} + \text{I}$ reaction (schematic). An inelastic scattering trajectory is shown. Lower panel: A contour map of the A band PES describing the half-collision with a typical dissociation trajectory.

shown in Fig. 2 (monomer). By gating the CH_3I^+ mass peak or the high-velocity z -component ($500 \leq v_z \leq 380 \text{ m/s}$) of I^+ KETOF distribution, while varying the pump–probe delay time, the dissociation dynamics was established.

The laboratory speed of I atoms is measured to be $\sim 400 \text{ m/s}$ from the clear splitting in the I^+ KETOF distribution. This value corresponds to the spin–orbit excited state $\text{I}(^2P_{1/2})$ dissociation channel and is in good agreement with those reported by others.¹⁵ The relatively smaller peaks at 550 m/s are the $\text{I}(^2P_{3/2})$ dissociation channel.¹⁸ As shown in Fig. 2, the I atom transient is clearly delayed from $t=0$ by $150 \pm 20 \text{ fs}$.¹⁹ The observed delay describes the coherent motion of the prepared wave packet on the repulsive (n, σ^*) potential surface and is the time needed to break the C–I bond. We have also measured the $\text{CH}_3\text{I}^{*\dagger}$ parent transient and found it to decay within our cross correlation response, in a time less than 50 fs . This is due to the fact that the wave packet prepared on the steep repulsive wall escapes out of the Franck–Condon region in a time much shorter than the nuclear recoil time. This dephasing, responsible for the severe spectral broadening, has no direct information on the direction or details of the motion.

From measurements of the separation time of I from the force field of CH_3 , 150 fs , and the terminal velocity, $v \sim 3700 \text{ m/s}$ or 0.037 \AA/fs , the nature of the repulsive force can be described. If the motion is purely kinetic, the two

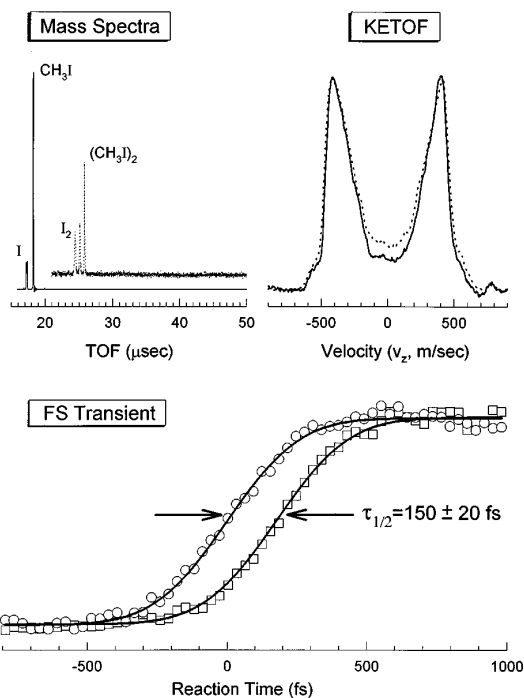


FIG. 2. Upper panel: (left) TOF mass spectra obtained for the monomer (solid line) and the monomer/dimer condition (dotted line). (right) The corresponding I^+ KETOF distributions taken at a delay time of $\sim 600 \text{ ps}$. Lower panel: The reference aniline 1+1 REMPI transient (\circ), *in situ*, defines the zero-of-time. The actual experimental transient (\square) was obtained by gating the highest velocity z -component ($500 \leq v_z \leq 380 \text{ m/s}$) under the monomer condition.

fragments will freely separate at $\sim 5.6 \text{ \AA}$. However, the repulsion involves a potential length scale L (for an exponential), and knowing the velocity and τ , we obtained an effective $L \sim 0.8 \text{ \AA}$ (from $\tau = (L/v) \ln(4E/V_f)$,²⁰ where E is the known available energy and V_f is the final value of the potential drop).

From the polarization dependence of the I atom KETOF distribution (with one average value of v), We also deduced the anisotropy parameter, $\beta \sim 1.85$, at 277 nm excitation, which is in good agreement with the values reported by Bersohn (1.81),¹⁶ Houston (1.8), Crim (1.9) and others¹⁵ (β was obtained from product angular distributions or from KETOF). From β , Bersohn deduced a lifetime of 70 fs .¹⁶ Kinsey and others^{14,15} have studied the molecular dynamics simulations of the reaction. The quantum wave-packet calculations by Guo and Schatz¹⁴ gave a 75 fs dissociation time for a C–I separation of $\sim 5 \text{ \AA}$. The 150 fs dissociation time reported here by direct clocking of the motion is longer than the β -deduced values. Measurements of the anisotropy (β) are sensitive only to the initial force (short distances) while real-time measurements probe the nuclear separation when fragments become free from the force field of each other (dissociation time). The theoretical values require further refinement of the PES.

THREE-CENTER BIMOLECULAR COLLISION

By gating the slow-velocity z -component ($0 \leq v_z \leq 250 \text{ m/s}$) of I^+ KETOF distribution (dimer), we obtained entirely

different results from those reported above. As shown in Fig. 3, when only the species $(\text{CH}_3\text{I})_2$ was present in the mass spectrum (see Fig. 2), the transient shows a delayed, slow rise behavior. The delay time is ~ 1.4 ps and the rise time is ~ 1.7 ps. This transient was repeated many times and is very reproducible. The observed ~ 1.4 ps delay time is striking and indicates that a coherent wave-packet motion well persisted in the entrance channel during the inelastic collision between CH_3I and I.

For the minimum energy dimer geometry calculated by Zeigler,²¹ with reference to the crystal structure,²² the I–I separation is estimated to be 3 Å and the structure is about 115° L-shaped with the two I atoms in proximity. The minimum energy structure of the complex is accordingly $\text{CH}_3\text{I}\cdots\text{I}$ (the I–I distance is >3 Å); generally for these types of systems, one expects two minima as, e.g., in the case of $\text{Cl} + \text{HCl}$ and $\text{I}\cdots\text{CH}_3\text{I}$ complexes.^{23,24} Hence, the initial fs pulse, which detaches the CH_3 group, suddenly turns the vdW attractive $\text{CH}_3\text{I}\cdots\text{ICH}_3$ force into a repulsive interaction on the ground state PES of $\text{CH}_3\text{I} + \text{I}$. The entire complex of CH_3I_2^+ recoils away from the CH_3 group. In the complex, the velocity of the I atom relative to the CH_3I molecule is small with an upper limit of 400 m/s, which corresponds to a maximum of 1.29 kcal/mol of collision energy.

As depicted in Fig. 1(A), the I atom first decelerates and then exchanges energy with CH_3I , and finally sticks to or separates from CH_3I depending on the strength of the repulsion and the initial translational energy. The latter, due to the large amplitude bending motion, could become less than the maximum available value. We have carried out preliminary MD simulations. Considering the large amplitude motion, a linear geometry was involved for simplicity. The CH_3I_2^+ vdW ($\text{CH}_3\text{I}\cdots\text{I}$) potential well was 1000 cm^{-1} deep and the equilibrium distance was 3.5 Å. These MD simulations show that the I atom takes ~ 2 ps to separate from the CH_3I moiety with an 8 Å I–I distance. The center-of-mass of CH_3I_2^+ moves ~ 5 Å, and because it has opposite velocity direction from the I atom (repulsive force) velocity in the complex the entire inelastic process slows down.

The 1.7 ps rise time of I atoms directly measures the lifetime of the CH_3I_2^+ complex trapped in the potential well (low v trajectories). It manifests any resonance motion in the CH_3I_2^+ complex during the energy redistribution. Molecular beam scattering experiments by Grice⁴ and Ross⁵ have shown a predominantly backscattered CH_3I from the reaction $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$ (at 2–3 kcal/mol collision energy), indicating a rebound repulsive release with the lifetime of the complex being comparable to or less than the rotational period. Our real-time results show the formation of a long-lived complex and indicate that the beam experiments were only sensitive to the short-lived, high-energy states of the complex. Syage's observed broad (I recoil) angular distribution is consistent with a long-lived complex.¹⁵ The formation of a complex in the inelastic $E \rightarrow V$ process of $\text{HI} + \text{I}$ (from HI dimers) has been shown recently by detecting the translational energy distributions of H atoms.²⁵ This is consistent with the above picture ($\text{CH}_3\text{I} + \text{I}$) and suggests a similar fs study of the HI system in this laboratory. It is interesting to

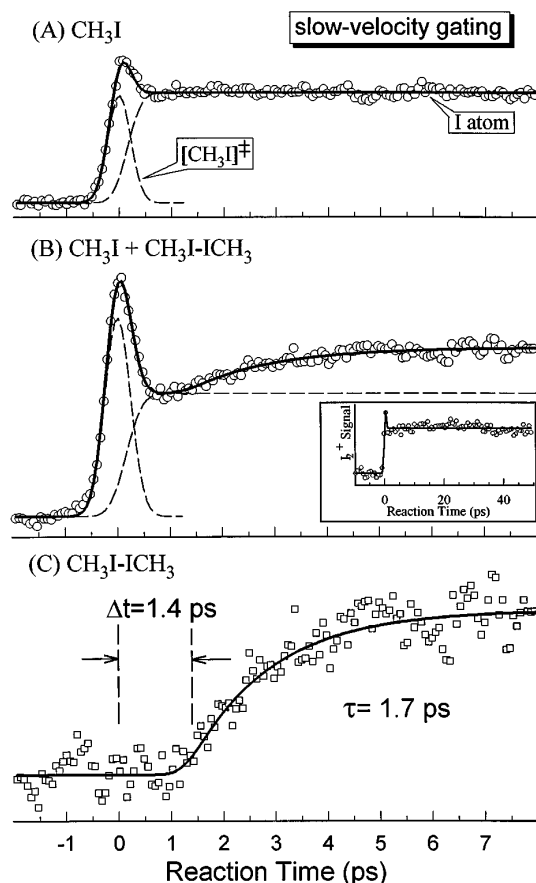


FIG. 3. (A) Femtosecond I^+ transient taken by gating the slow-velocity z -component ($0 \leq v_z \leq 250$ m/s), under the monomer condition. The transient was best fitted by two components (dashed lines), consistent with results in Fig. 2: a peak at time zero, from the fragmentation of CH_3I^+ , and a shifted (150 fs) step-function rise from the dissociation product. (B) I^+ transient obtained under the same conditions as in (A) except for the dimer condition. The dashed lines (peak+plateau), similar to (A), are the contributions from the monomer dissociation. The apparent rise signal at longer times, which is absent in (A), gives the dimer transient. The I_2^+ transient is shown in the inset. The rise is prompt within 500 femtoseconds. (C) The transient response (\square) of $(\text{CH}_3\text{I})_2$, after correction for the monomer in (B), was best fitted by a delayed single exponential rise.

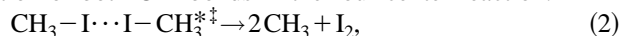
note that the lifetimes of excited-state complexes ($\text{Hg}^* \cdot \text{N}_2$) in vdW wells have been reported to be of similar magnitude (2–5 ps).²⁶

FOUR-CENTER BIMOLECULAR REACTION

For the three-center reaction dynamics described above, at the translational energy of our experiments, the wave packet cannot cross the barrier to $\text{CH}_3 + \text{I}_2$ formation. By using 304 nm as a pump, this reactive channel is still *not* open even for two-photon excitation, where the C–I bond breakage is still on the fs time scale.²⁷ This is because the detached CH_3 takes up most of the available energy ($m_1 E_{\text{avt}}/m_{\text{CH}_3\text{I}}$) either for the $\text{I}(^2P_{3/2})$ or $\text{I}(^2P_{1/2})$, as mentioned before. The reaction of $\text{CH}_3\text{I} + \text{I}(^2P_{3/2}) \rightarrow \text{I}_2 + \text{CH}_3$ is endothermic by 17.5 kcal/mol. [The channel of $\text{CH}_3\text{I} + \text{I}(^2P_{1/2})$, although it exceeds the endothermicity, is shown to proceed through the inelastic collision by $E \rightarrow V$ transfer to form $\text{CH}_3\text{I}(v) + \text{I}(^2P_{3/2})$.²⁸] The fact that we do

observe the I_2 formation under the dimer condition, indicates a “four-center” mechanism. As shown in the inset of Fig. 3(B), the build up of I_2 is very fast, in less than 500 fs. With a 304 nm pump pulse (two photons), the I_2 molecule can be formed in the electronically excited B state and detected by a 1+1 REMPI process (277 nm). Indeed the power dependence of the pump shows a quadratic behavior. No attempt yet was made to examine the ground state I_2 formation, observed in one-photon A-band promotion.²⁹

The key for the formation of I_2 is the cooperative nuclear motion of both C–I bonds in the four-center reaction:



a Bodenstein-type reaction.³⁰ Because the equilibrium distance of I_2 is 2.6 Å and the separation of I–I in the dimer is already about 3 Å, the I_2 molecule is formed promptly. Such I_2 formation has been studied in CW experiments^{21,29,31} and with 10 ps resolution.³² The fs I_2 dynamics reported here can be rationalized using frontier orbitals. The initial fs one-electron promotion makes the lowest unoccupied molecular orbit/highest occupied molecular orbit (LUMO/HOMO) interaction effective to create an I–I bond with the in-phase σ^* orbital ($n \rightarrow \sigma^*$ excitation) or s or p orbital (Rydberg excitation) combination on the two I atoms. Donaldson and co-workers²⁹ proposed a modified exciton model. After the excitation of a CH_3I moiety to the A continuum or to the Rydberg state, a partial charge transfer occurs from one I end to the other. This process results in some anion-type character with the C–I bond now experiencing a repulsive force.

The consequence of the orbital interactions is to form the I–I bond on the time scale of the C–I breakage which as reported here is 150 fs (for Rydberg excitation is similar),²⁷ consistent with the results in Fig. 3 for I_2 production. The I_2 formation, which may be coherent, as shown in the case of molecular photodissociation (CH_2I_2),³³ has also been observed in the photodissociation of the HI dimer,^{34,35} and again is a four-center reaction. Polanyi's group³⁶ observed the formation of Cl_2 and Br_2 by photoinitiating reactions of $2HX$ ($X=Cl$ and Br) on LiF surfaces. This surface aligned formation of X_2 is a four-center reaction. The chemistry in these aligned complexes and surfaces is novel and we plan further studies in this area.

In conclusion, the studies reported here provide direct resolution of the dynamics of the C–I bond breakage (time, velocity, and anisotropy), the inelastic process of CH_3I+I and the reactive four-center I_2 production. The results indicate a repulsion length scale of 0.8 Å (for CH_3I dissociation) in 150 fs, a coherent inelastic process (1.4 ps) with a long-lived collision complex (1.7 ps), and a cooperative I_2 formation in less than 500 fs. Extension of the fs detachment approach should now cover negative ions,³⁷ adding to Neumark's CW experiments³⁸ the fs resolution.

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¹⁸The dominant channel involves the $I(^2P_{1/2})$, as evident from the strong KETOF peaks for $I(^2P_{1/2})$ relative to the weaker ones for $I(^2P_{3/2})$. Even if some trajectories involve the $I(^2P_{3/2})$ channel, the collision energy is only different from the $I(^2P_{1/2})$ by 1.15 kcal/mol.

¹⁹A very small portion of I^+ signal at $t=0$ from the CH_3I^+ fragmentation was corrected. This is because the ionization potential of CH_3I is 9.54 eV and the absorption by CH_3I^{\ddagger} of three probe photons causes some fragmentation to $I^+ + CH_3$ and $CH_3^+ + I$.

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